PERGAMON

Solid State Communications 117 (2001) 537–541

solid state communications

www.elsevier.com/locate/ssc

Hopping conduction through the 2s states of copper acceptors in uniaxially stressed germanium

O.D. Dubon[a,b,*], H.H. Silvestri[a,b], W. Walukiewicz[b], E.E. Haller[a,b]

[a]*Department of Materials Science & Engineering, University of California, Berkeley, CA 94720, USA*
[b]*Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*

Received 14 September 2000; received in revised form 13 November 2000; accepted 20 November 2000 by H. von Löhneysen

Abstract

We have studied hopping conduction in uniaxially stressed Cu-doped Ge. The electronic ground state of neutral Cu acceptors, normally accommodating three 1s holes, undergoes a transformation to a $1s^2 2s^1$ configuration with the application of uniaxial stress greater than 4 kbar. Upon undergoing this transformation, the copper acceptors form a system of lithium-like impurities in which hopping transitions of carriers take place through 2s rather than 1s states. The significant overlap between the more extended 2s wavefunctions located on different sites results in a decrease of the resistivity in the hopping regime by eight orders of magnitude. Good agreement was obtained between the experimental results and our calculations.

Keywords: A. Semiconductors; C. Impurities in semicondutors; D. Electronic transport

PACS: 71.55.−i; 72.20.Ee; 72.80.Cw

In semiconductors, dopants make up a system of Coulomb centers whose interactions can be tuned through their concentration. At low densities these impurities are spatially and electronically isolated from each other, and their electronic states are characterized by discrete energy levels. At higher concentrations on-site electron–electron interactions and overlap between wavefunctions of neighboring centers lead to impurity-related energy bands, known as the upper and lower Hubbard bands in the Mott-Hubbard framework [1]. In an uncompensated semiconductor at temperatures approaching absolute zero, essentially all states of the lower Hubbard band are filled, and impurity conduction arises from carriers that are thermally excited to delocalized states of the upper Hubbard band. However, the omnipresence of compensating impurities (e.g. Sb donors in *p*-type Ge) leads to charge transport in the lower Hubbard band by phonon-mediated hopping of carriers through a network of localized states formed by ionized dopants.

In moderately doped semiconductors nearest-neighbor hopping (NNH) is the most widely observed form of electronic conduction at liquid helium temperatures. The electrical resistivity associated with this transport process has the form $\rho_{NNH} = \rho_3 \exp(\epsilon_3/kT)$ where ϵ_3 is the activation energy for hopping and ρ_3 is the temperature independent prefactor which, to a large extent, determines the magnitude of the resistivity [1–4]. The activation energy ϵ_3 corresponds to the shift of the Fermi energy from the isolated-dopant level due to Coulomb interactions. The pre-exponential term ρ_3 contains information on the hopping transition probability, which is a function of the long-range overlap between dopant wavefunctions. While ϵ_3 and ρ_3 are very sensitive to majority dopant density, ρ_3 also depends strongly on the spatial extent of the dopant electronic ground state. This has been demonstrated through investigations in which uniaxial stress [5,6] or a magnetic field [6,7] is used to change the shape of the wavefunctions of shallow dopants. For example, the application of uniaxial compression to Ga-doped Ge single crystals reduces the magnitude of ρ_3 by as much as a factor of 50. Uniaxial stress extends the 1s wavefunction of Ga acceptors leading to increased overlap and a higher probability for a hopping transition [8]. A magnetic field produces the opposite effect and results in an increase of the resistivity.

Thus far, investigations of hopping transport in doped

* Corresponding author.
E-mail address: addubon@socrates.berkeley.edu (O.D. Dubon).

0038-1098/01/$ - see front matter
PII: S0038-1098(00)00499-3

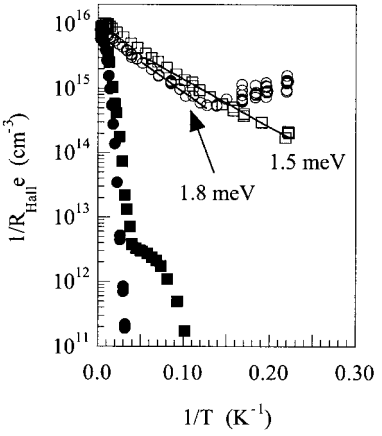

Fig. 1. Temperature dependence of the inverse Hall coefficient R_{Hall} (multiplied by the electron charge $e = 1.6 \times 10^{-19}$ C) for two samples. The squares correspond to a sample with a copper concentration of 7.9×10^{15} cm^{-3} and a net shallow acceptor concentration of 3×10^{12} cm^{-3} while the circles refer to a sample with 6.5×10^{15} cm^{-3} Cu acceptors and 3×10^{14} cm^{-3} compensating Sb donors. The solid symbols were obtained with zero-stress applied. The clear symbols represent data obtained with an applied uniaxial stress greater than 4 kbar.

semiconductors have been constrained by the hydrogen-like nature of all shallow dopants which, regardless of their chemical identity, are characterized by a ground state wherein holes occupy 1s states exclusively. Here we show that changing the nature of the electronic ground state of dopants has a dramatic effect on hopping conduction. The application of a sufficiently large uniaxial stress to Cu-doped germanium transforms the copper acceptors into a system of lithium-like dopants in which holes reside in 2s states. The significantly larger size of the 2s wavefunction results in a decrease of the resistivity due to hopping conduction of eight orders of magnitude.

In the absence of uniaxial stress, the fourfold degeneracy of the valence-band edge of Ge allows for the accommodation of three 1s holes in the ground state of neutral copper acceptors. We have previously shown that the ground state of this triple acceptor is transformed from a pseudo Li^0, $1s^3$-like configuration to a normal Li^0, $1s^2 2s^1$-like configuration upon the application of uniaxial stress greater than 4 kbar [9]. Experimentally this ground-state transformation is manifested as a pressure-induced shift of the photoionization energy of neutral copper acceptors from a zero-stress value of 43.2 meV to a nearly constant value of 17 meV above 4 kbar.

The transformation of the ground state of Cu acceptors leads to the formation of Hubbard bands that are well separated from the valence band edge [10]. These bands are constructed from the highly extended 2s wavefunctions of the $1s^2 2s^1$-like configuration. The lower Hubbard band is formed from the ground state of neutral Cu acceptors while the upper Hubbard band consists of states associated with the overcharged acceptor (Cu^+). Therefore, the upper Hubbard band lies closer to the valence band edge at a higher hole energy than the lower Hubbard band. This is completely analogous to the formation of Hubbard bands from donor states in n-type semiconductors.

The concentration of holes in the upper Hubbard band is thermally activated. The decrease in activation energy of the hole concentration with increasing copper acceptor density in highly stressed Ge corresponds to the closure of the energy gap between the lower and upper Hubbard bands. More recently we have analyzed the transport properties of holes in the upper Hubbard band, a study made possible by the isolation of the 2s states from the valence band edge [11].

The samples in this study were prepared by diffusing copper into Ge single crystal wafers as described elsewhere [9]. Processed wafers were cut into $1 \times 1 \times 5$ mm^3 parallelipipeds with all resulting surfaces being ⟨001⟩-oriented. Hall effect measurements on copper-diffused Ge crystals show that the homogeneity of the spatial distribution of copper acceptors in the samples should be better than 2%. Some samples were produced from a wafer having a grown-in Sb concentration, N_{Sb}, of 3×10^{14} cm^{-3}. Uniaxial stress was applied parallel to the long axis of the bar-shaped samples using a leaf-spring/piston apparatus. Low-temperature electrical resistivity and Hall effect measurements were performed on these samples. Additional resistivity measurements were performed on uniaxially stressed $1 \times 1 \times 1$ mm^3 samples.

Fig. 1 shows the dependence of the Hall coefficient (R_{Hall}) on temperature for unstressed and uniaxially stressed crystals. The circles refer to a sample with a Cu acceptor concentration, N_{Cu}, of 6.5×10^{15} cm^{-3} and 3×10^{14} cm^{-3} compensating Sb donors. The compensation ratio, equal to N_{Sb}/N_{Cu}, has a magnitude of 0.046, which satisfies the "weak compensation" condition $N_{Sb}/N_{Cu} \ll 1$ [4,12]. In general, the ordinate corresponds to the hole concentration. The change in slope from negative to positive observed under a large applied uniaxial stress (clear circles) results from a change in hole conduction mode from upper Hubbard band transport to hopping conduction in the lower Hubbard band. The ordinate is no longer a measure of the hole concentration in the hopping regime [13]. For comparison, the measurements designated by squares were obtained for a sample with 7.9×10^{15} cm^{-3} Cu acceptors and a net shallow acceptor concentration of 3×10^{12} cm^{-3}. In this Ge crystal the copper acceptors are not compensated.

In the temperature range where upper Hubbard band transport is observed, the hole concentration displays an Arrhenius behavior with an activation energy that corresponds to the Hubbard gap. For the sample in which copper acceptors are not compensated, the Hubbard gap is exhibited down to the lowest temperatures. An increase in the density of Cu acceptors from 6.5×10^{15} to 7.9×10^{15} cm^{-3} lowers the activation energy from approximately 1.8 to 1.5 meV.

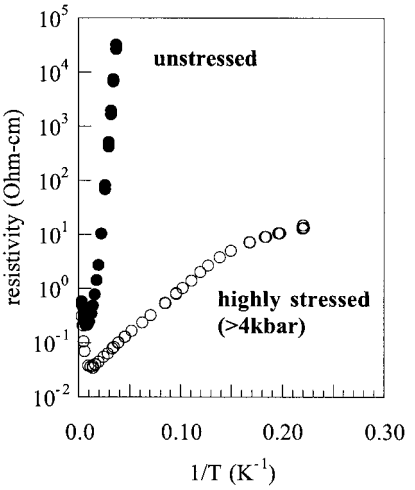

Fig. 2. Temperature dependence of the resistivity for a Ge single crystal containing 6.5×10^{15} cm^{-3} Cu acceptors and 3×10^{14} cm^{-3} compensating Sb donors. Without stress the resistivity exhibits a strong temperature dependence due to the "freeze-out" of holes onto the copper acceptor level (filled circles). The application of large uniaxial stress leads to impurity band conduction which is characterized by a weaker temperature dependence of the resistivity (clear circles). At the lowest temperatures, the resistivity shows a further weakening in temperature dependence due to the transition from hole transport in the upper Hubbard band at the higher temperatures to hopping conduction in the lower Hubbard band.

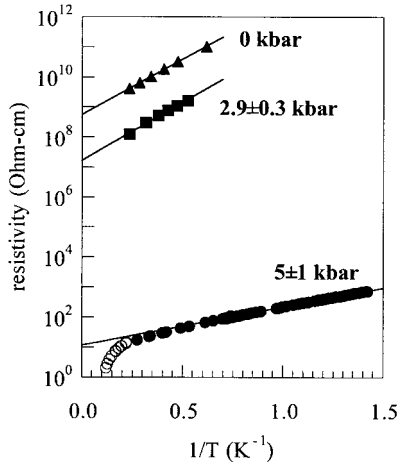

Fig. 3. Temperature dependence of the resistivity of a Ge crystal containing 6.5×10^{15} cm^{-3} Cu acceptors and 3×10^{14} cm^{-3} compensating Sb donors for three conditions of stress: 0 kbar (triangles), 2.9 ± 0.3 kbar (squares), and 5 ± 1 kbar (solid circles). While the application of 2.9 kbar reduces the resistivity by a factor of 35, a further increase of stress by only 2 kbar results in an extraordinary decrease of the resistivity by six orders of magnitude. Resistivity measurements obtained under uniaxial stress and shown in Fig. 2 are also presented here for reference (clear circles).

These energies are consistent with our previous measurements and calculations [10].

We have measured the resistivity of these samples over the temperature range of 300–4.6 K. The measurements for the sample containing compensating Sb donors are presented in Fig. 2. In the absence of stress, the resistivity increases with decreasing temperature with an activation energy of approximately 45 meV corresponding to the binding energy of holes by the neutral copper acceptors. The resistivity of the highly stressed sample exhibits a weaker temperature dependence that further weakens at the lowest temperatures. This change in thermal activation corresponds to the transition from upper Hubbard band transport to hopping conduction also observed in the Hall effect measurements.

Two-point resistivity measurements were performed on the crystal containing Sb donors at temperatures below 4.6 K for three values of applied stress: 0, 2.9 ± 0.3, and 5 ± 1 kbar. The data are shown in Fig. 3. A uniaxial stress of 2.9 kbar results in a decrease of ρ_3 from a zero-stress value of 5.6×10^8 to 1.6×10^7 Ω cm. The reduction of the prefactor is consistent with previous results for Ga-doped Ge [5,6]. The activation energy ϵ_3 is essentially unchanged — 0.73 meV at 0 kbar compared to 0.74 meV at 2.9 kbar. The application of 5 kbar further reduces the magnitude of ρ_3 to 11.3 Ω cm. This dramatic decrease by six orders of magnitude with an increase in uniaxial stress by only 2 kbar is accompanied by a reduction in ϵ_3 by a factor of 3 to a value of 0.25 meV. We propose that the high-stress, Li^0-like configuration of copper acceptors is at the heart of the extraordinary difference in magnitude of the hopping resistivity.

We have estimated the magnitude of ρ_3 for a lithium-like dopant following the method used previously for hydrogenic impurities [4,12]. This pre-exponential term is inversely proportional to the probability for a hopping transition. Therefore, ρ_3 has the following form for the 2s holes associated with the high-stress, copper-acceptor ground state:

$$\rho_3 = \rho_0 \left| \int \mathrm{d}\mathbf{r} u_{2s}^{i}(\mathbf{r}) u_{2s}^{j}(\mathbf{r}) \right|^{-2} \tag{1}$$

where $u_{2s}(\mathbf{r})$ is the radially dependent part of the 2s wavefunction at sites i and j. In our analysis $u_{2s}(\mathbf{r})$ has the form [10,14]:

$$u_{2s}(\mathbf{r}) = C\mu^{5/2}\left[\frac{\mathbf{r}}{a_B}\exp\left(-\frac{\mu\mathbf{r}}{a_B}\right) - \left(\frac{3A}{\mu}\right)\exp\left(-\frac{\mu b\mathbf{r}}{a_B}\right)\right] \tag{2}$$

where a, b and μ are the variation parameters, $A = (a+b)^3/(a+1)^4$, and C is a normalization constant. The effective hydrogenic Bohr radius a_B is approximately equal to 64 Å corresponding to an effective Bohr energy of 7 meV associated with acceptors in uniaxially stressed Ge — 4 kbar applied along a ⟨001⟩ direction. For the Li^0-like copper ground-state, $a = 4.03$, $b = 3.19$ and $\mu = 1.3$ [10].

Because $u_{2s}(\mathbf{r})$ is governed at large distances by the first term in the square brackets, we have calculated ρ_3 using only this term [15]. Similar analysis was successfully applied to a system of hydrogen-like dopants, where the long-range characteristics of the dopant wavefunction were found to determine the hopping transition probability [8,12]. We thus arrive at the analytical form of ρ_3:

$$\rho_3 = \rho_0[\exp(-w)(\tfrac{1}{45}w^4 + \tfrac{1}{9}w^3 + \tfrac{4}{9}w^2 + w + 1)]^{-2} \quad (3)$$

where $w = \mu\mathbf{r}_{ij}/a_B$ and $\mathbf{r}_{ij}$ is the average impurity separation which is approximately equal to $(3/(4\pi N_{Cu}))^{1/3}$. In hopping transport the length scale of importance is the average distance between centers at the percolation threshold, r_c, which replaces $\mathbf{r}_{ij}$ in Eq. (3) [4]. This critical distance is similar in magnitude to $\mathbf{r}_{ij}$ and is given by $r_c = \beta_0^{1/3}\mathbf{r}_{ij}$ where β_0 is a constant on the order of unity.

It has been previously found that for hopping conduction in unstressed copper-doped germanium crystals, $\rho_3 = \rho_0 \exp(2/(a_{Cu}N_{Cu}^{1/3}))$ where a_{Cu} is the effective hopping radius for copper acceptors and has a value of 47 Å [12,16]. Because ρ_3 has a magnitude of $5.6\times10^8\,\Omega\,\mathrm{cm}$ for the unstressed crystal, the constant ρ_0 equals $0.070\,\Omega\,\mathrm{cm}$. Using this value, we find that the stress-induced magnitude of ρ_3 given by Eq. (3) is $4.4\,\Omega\,\mathrm{cm}$ for a copper concentration of $6.5\times10^{15}\,\mathrm{cm}^{-3}$ and β_0 equal to one. The calculated magnitude of ρ_3 is in good agreement with the experimentally observed value of $11.3\,\Omega\,\mathrm{cm}$. Thus, the decrease by eight orders of magnitude of the resistivity reflects the remarkable increase in the hopping transition probability for 2s holes of the $1s^22s^1$-like ground state compared to 1s holes of the $1s^3$-like Cu configuration in the unstressed crystal.

The invariance of ϵ_3 with the application of 2.9 kbar is expected. With a hole binding energy of 23 meV for an applied stress of 2.9 kbar,[9] the copper-acceptor wavefunction remains compact minimizing effects due to wavefunction overlap. In the absence of significant overlap, ϵ_3 depends only on the concentrations of majority and minority impurities with corrections to account for a non-random distribution of the minority impurities [4,12].

The significant decrease of the activation energy from 0.74 to 0.25 meV upon the further application of stress is a direct consequence of the transformation of copper acceptors into a system of lithium-like impurities. The more extended 2s wavefunctions located on different sites overlap significantly resulting in an increased width of the impurity band. In effect, a Cu acceptor concentration of $6.5\times10^{15}\,\mathrm{cm}^{-3}$ is orders of magnitude below the critical concentration for the metal-insulator transition (MIT) in unstressed Ge but is within a factor of three of the critical concentration upon the application of a sufficiently large uniaxial stress (>4 kbar). A decrease of ϵ_3 has also been observed in Ge as a function of increasing shallow impurity concentration [12]. Significant wavefunction overlap — in one case due to a ground-state transformation and in the other case due to a reduction in the separation between impurities — facilitates electron–electron correlations. These enable processes such as multi-electron hopping which are characterized by a reduced activation energy [6,7].

Deviation from an Arrhenius behavior of the resistivity of the sample stressed to 5 kbar (Fig. 3) suggests that a combination of hopping mechanisms, nearest-neighbor hopping and variable-range hopping (VRH) of the Efros-Shklovskii type, is at play. In this case the resistivity due to hopping, ρ_{hop}, is given by

$$\rho_{hop} = \left(\frac{1}{\rho_{NNH}} + \frac{1}{\rho_{VRH}}\right)^{-1} \quad (4)$$

where

$$\rho_{VRH} = \rho_{01}\exp\left(\frac{T_0}{T}\right)^{1/2}. \quad (5)$$

In the temperature range between 4.0 and 0.7 K, ρ_{hop} is well described by Eq. (4) if the pre-factor ρ_0 and activation energy ϵ_3 associated with nearest-neighbor hopping are $18.2\,\Omega\,\mathrm{cm}$ and 0.28 meV, respectively, while $\rho_{01} = 1.35\,\Omega\,\mathrm{cm}$ and $T_0 = 33.0$ K. The magnitude of the parameters associated with NNH do not differ significantly from the corresponding values which were obtained by considering only NNH ($\rho_0 = 11.3\,\Omega\,\mathrm{cm}$ and $\epsilon_3 = 0.25$ meV). Fitting the data by VRH alone is inadequate. Further investigations are necessary to better understand the actual mechanism(s) involved.

In summary, we have observed hopping conduction through the 2s states of Cu acceptors in uniaxially stressed Ge. The stress-induced change of the wavefunction involved in the hopping process from 1s to 2s results in a dramatic reduction of the low-temperature resistivity by many orders of magnitude. With a $1s^22s^1$ ground state at high stress, Cu acceptors form a system of lithium-like impurities characterized by an activation energy for hopping conduction of 0.25 meV, a Hubbard gap of 1.8 meV and a hole binding energy of 17 meV for samples used in this study. The mechanisms of charge transport are clearly differentiated due to the large differences in the activation energies. The properties of impurity bands as a function of dopant concentration on the insulating side of the MIT can be studied without interference of valence band conduction. Moreover, processes associated with the lower Hubbard band including the evolution of the Coulomb gap can be separated from effects associated with the upper Hubbard band. The large binding energy combined with the extended nature of the 2s wavefunctions provides an unprecedented opportunity for comprehensive investigations of the electronic transport processes in impurity bands.

Acknowledgements

The authors thank J.W. Beeman for technical support.

This research was supported in part by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences Division of the US Department of Energy, under contract No. DE-AC03-76SF00098.

References

[1] N.F. Mott, E.A. Davis, Electronic Processes in Non-crystalline Semiconductors, Clarendon Press, Oxford, 1979.
[2] H. Fritzsche, M. Cuevas, Phys. Rev. 119 (1960) 1238.
[3] A. Miller, E. Abrahams, Phys. Rev. 120 (1960) 745.
[4] B.I. Shklovskii, Sov. Phys. Semicond. 6 (1973) 1053 [Fizika i Tekhnika Poluprovodnikov 6 (1972) 1197].
[5] F.H. Pollak, Phys. Rev. 138 (1965) A618.
[6] J.A. Chroboczek, H. Fritzche, C.-L. Jiang, M. Pollak, R.L. Wild, Philos. Mag. B 44 (1981) 685.
[7] M.L. Knotek, Phys. Rev. B 16 (1977) 2629.
[8] R. Buczko, J.A. Chroboczek, Philos. Mag. B 50 (1984) 429.
[9] O.D. Dubon, J.W. Beeman, L.M. Falicov, H.D. Fuchs, E.E. Haller, C. Wang, Phys. Rev. Lett. 72 (1994) 2231.
[10] O.D. Dubon, W. Walukiewicz, J.W. Beeman, E.E. Haller, Phys. Rev. Lett. 78 (1997) 3519.
[11] W. Walukiewicz, O.D. Dubon, H.H. Silvestri, E.E. Haller, Phys. Status Solidi B 210 (1998) 253.
[12] B.I. Shklovskii, A.L. Efros, Electronic Properties of Doped Semiconductors, Solid State Series, Vol. 45, Springer, Berlin, 1984.
[13] E.A. Davis, W.D. Compton, Phys. Rev. 140 (1965) A2183.
[14] J.C. Slater, Quantum Theory of Atomic Structure, Vol. 1, McGraw-Hill, New York, 1960, p. 348.
[15] J.C. Slater, Quantum Theory of Molecules and Solids, Vol. 1, McGraw-Hill, New York, 1963, p. 25.
[16] B.V. Rollin, J.P. Russell, Proc. Phys. Soc., London 81 (1965) 571.